

Zirconium (IV) Oxide Coated Silica Gel Surface as a Base for Copper Hexacyanoferrate Immobilization

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O complexo de hexacianoferrato de cobre foi imobilizado sobre um filme fino de ZrO_2 enxertado na superfície da sílica gel. A baixa densidade superficial das espécies químicas sugere que o complexo está altamente disperso na superfície (área específica de $420 \text{ m}^2 \text{ g}^{-1}$) como pequenas ilhas. O eletrodo de pasta de carbono do material mostrou, pela técnica de voltametria cíclica, que o mesmo (material) apresenta uma permeação seletiva aos íons Li^+ , Na^+ , K^+ e NH_4^+ , de acordo com o tamanho relativo do diâmetro dos íons hidratados. Observou-se um bloqueio do processo redox para Li^+ e Na^+ , enquanto para K^+ e NH_4^+ os potenciais médios foram observados em 0,69 V e 0,75 V, respectivamente. A dependência do potencial de pico com a concentração dos eletrólitos suporte mostrou um comportamento *quasi* nernstiano para os íons K^+ e NH_4^+ .

Copper hexacyanoferrate complex was immobilized on a thin ZrO_2 film coated SiO_2 surface. The small surface density of the chemical species suggested that the complex was highly dispersed on the surface (specific surface area of $420 \text{ m}^2 \text{ g}^{-1}$) like small islands. Cyclic voltammetric data from a carbon paste electrode made with the material showed a selective permeation toward Li^+ , Na^+ , K^+ and NH_4^+ , according to their hydrated diameter size. The redox process was blocked for Li^+ and Na^+ , while for K^+ and NH_4^+ ions the midpoint potentials were 0.69 V and 0.75 V, respectively. The dependence of peak potential on the concentrations of the supporting electrolytes indicated a *quasi* Nernstian behavior for the K^+ and NH_4^+ ions.

Keywords: copper hexacyanoferrate, thin ZrO_2 film on SiO_2 surface, copper hexacyanoferrate immobilized on ZrO_2/SiO_2 , cyclic voltammetry study of copper hexacyanoferrate immobilized on ZrO_2/SiO_2

Introduction

Thin films of transition metal hexacyanoferrate coatings on metal electrode surfaces have become of particular interest in recent years. In the bulk phase these mixed valence complexes constitute an important class of compounds of the composition $M_m[Fe^k(CN)_6]_n$, where M is a transition metal, and j and k are the different formal oxidation numbers¹. On the electrode surface the films of these compounds have a defined structure and present selective permeation toward alkali metal ions²⁻¹⁴. Good adhesion has been achieved using platinum, gold or glassy carbon disk as the supporting material.

Thin films of metal oxide coatings on heterogeneous silica gel surfaces have also been used as chemically modified electrodes¹⁵. In aqueous suspension, the oxide surfaces are generally electrically charged and at a pH below or above the isoelectric point they can adsorb charged species by an ion exchange process¹⁶. Transition metal hexacyan-

oferrates have been immobilized on the surface of oxides and the ion paired species strongly adhered to the surface at low solution pH values¹⁷⁻²². Dispersed oxides on silica surfaces have an important effect on the process of the hexacyanoferrate film formation because the interaction with the charged surface limits the mobility of the adsorbate. However, the electrodes made by these materials are normally, very chemically stable.

Since the process of film formation on the surface of porous materials is not well known, and considering the potential use of these materials as electrochemical sensors, the preparation and selective permeation property of copper hexacyanoferrate film adsorbed on silica gel surface coated by zirconium (IV) oxide were studied in this work.

Experimental

Preparation of ZrO_2 coated SiO_2

About 50 g of Merck silica gel, having a specific surface area (S_{BET}) of $500 \text{ m}^2 \text{ g}^{-1}$ and an average pore diameter of

6 nm, was added to 300 mL of 0.2 M ZrOCl_2 solution. The mixture was heated at about 300 K for 6 h under stirring. The solid was decanted, washed with water until a negative test for the chloride ion was obtained, and then dried in an oven at 423 K. The quantity of zirconium in the material, designated as $\text{ZrO}_2/\text{SiO}_2$, was determined by X-ray fluorescence analysis.

Copper hexacyanoferrate was immobilized on $\text{ZrO}_2/\text{SiO}_2$ by two experimental procedures:

Procedure 1. About 0.5 g of $\text{ZrO}_2/\text{SiO}_2$ was added to 100 mL of potassium hexacyanoferrate 10^{-2} M solution (pH 1). The mixture was stirred for 15 min. The resulting solid was added to 100 mL of 10^{-2} M Cu^{2+} solution and shaken for 15 min and then filtered, washed with water and air dried at room temperature.

Procedure 2. About 1.5 g of $\text{ZrO}_2/\text{SiO}_2$ was added to 100 mL of 0.03M CuCl_2 solution. The pH of the solution was raised by adding 0.5 g of sodium acetate and the mixture was stirred for 5 min. The resulting solid was filtered, washed with water and air dried. About 0.35 g of this material was added to 50 mL of 10^{-3} M potassium ferrocyanide solution, and the mixture was stirred for about 5 min and then filtered, washed with water and dried under vacuum at room temperature.

The quantities of Fe and Cu were determined by X-ray fluorescence analysis. The results are presented in Table 1.

Spectrophotometric measurements

The electronic absorption spectra of the solids were measured by adding the material to spectral grade CCl_4 using a quartz window with a 1 mm path length. Under these experimental conditions light scattering by the solid particles was minimum since the refractive index of CCl_4 is very close to that of SiO_2 , and therefore good quality spectra were obtained. A Beckman DU 640 spectrophotometer, was used.

Cyclic voltammetry measurements

The cyclic voltammetry (CV) measurements were made with a carbon paste electrode made from the material following a procedure described elsewhere¹⁷. This electrode was used as the working electrode, a platinum wire was used as the auxiliary electrode and a saturated calomel electrode (SCE) was the reference electrode. All measurements were made under highly pure nitrogen atmosphere using a potentiostat PAR 264 (EG & G) connected to a X-Y recorder.

Infra-red spectra

Infra-red spectra of the samples were recorded on a Perkin Elmer FT-IR 1600 spectrophotometer using a pressed disk made from the material.

Table 1. Chemical analyses of $\text{ZrO}_2/\text{SiO}_2/\text{CuHCF}$.

| Samples ^a | Fe / $\mu\text{mol g}^{-1}$ | Cu / $\mu\text{mol g}^{-1}$ | Cu/Fe |
|----------------------|-----------------------------|-----------------------------|-------|
| a | 69 | 15 | 0.22 |
| b | 57 | 22 | 0.38 |
| c | 53 | 23 | 0.43 |
| d | 38 | 22 | 0.59 |
| e | 23 | 91 | 4.0 |

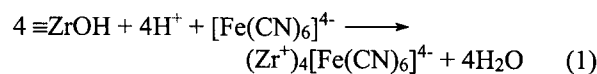
^aExcept sample e, all others (a-d) were prepared according to Procedure 1.

Results and Discussion

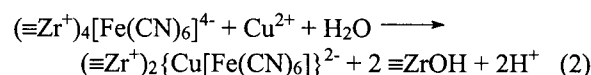
Preparation of the material

To describe the reactions that occur on the surface, a set of formal reaction equations can be written. Clearly they do not correspond to an exact description, but are rather an approximate representation of the reactions.

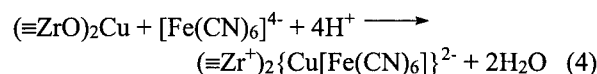
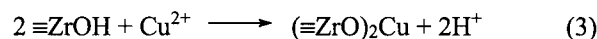
In the first procedure, HCF is adsorbed on the $\text{ZrO}_2/\text{SiO}_2$ surface at a lower solution pH according to the reaction²³:



where $\equiv \text{ZrOH}$ stands for hydrated zirconium (IV) attached to the SiO_2 surface. Upon the addition of this material to a solution of Cu^{2+} , the formation of a dark brown complex on the surface is observed. The reaction that occurs can be represented by the equation:



In the second procedure, the adsorption of Cu^{2+} by $\text{ZrO}_2/\text{SiO}_2$ and the further reaction with hexacyanoferrate can be represented by the equations:



The chemical species formed on the surface are the same in both experimental procedures, but the ratio Cu/Fe < 1 is obtained following Procedure 1 and Cu/Fe > 1 is obtained by following Procedure 2 (See Table 1 for chemical analyses). For samples prepared using Procedure 1, there is an excess of hexacyanoferrate on the surface that may decompose with time, as will be seen later.

Characteristics of the material

The infra-red spectra of samples were obtained in order to get more information on how the chemical species interact with the surface. The CN stretching (νCN) fre-

Table 2. CN stretching bands (CN) for HCF^a and CuHCF^b on ZrO₂/SiO₂

| Samples | $\nu_{\text{CN}} / \text{cm}^{-1}$ |
|---|------------------------------------|
| K ₄ [Fe(CN) ₆] | 2040 |
| Cu ₂ [Fe(CN) ₆] | 2100 |
| ZrO ₂ /SiO ₂ /HCF | 2080 |
| ZrO ₂ /SiO ₂ /CuHCF | 2095 ^c |

^aHCF = hexacyanoferrate; ^bCuHCF = copper hexacyanoferrate; ^caverage frequency for samples a-e.

quencies are listed in Table 2. The ν_{CN} frequency is observed at 2080 cm⁻¹ for ZrO₂/SiO₂/HCF, while for K₄[Fe(CN)₆] it is observed at 2040 cm⁻¹. For ZrO₂/SiO₂/CuHCF the ν_{CN} band is observed at 2095 cm⁻¹, practically the same frequency observed for Cu₂[Fe(CN)₆]. The structure of this complex shows that the Cu ion is coordinated with the cyanide nitrogen atom^{24,25}. It is known that for the interaction of cyanide nitrogen through electron density donation to a Lewis acid the stretching force constant of the CN bond increases, raising the corresponding frequency²⁶. In the case of ZrO₂/SiO₂/HCF although the interaction of HCF with the positively charged surface is supposed to be electrostatic, leaching the anion from the surface through an ion exchange reaction by treatment with concentrated acid solution is very difficult. The strong adherence of HCF to the ZrO₂/SiO₂ surface is presumably due to the direct interaction of cyanide nitrogen with uncoordinated Lewis acid sites ($\equiv\text{Zr}^+$) at the solid-solution interface.

Although the resulting CuHCF complex on the surface is the same in both preparation methods, an excess of unreacted HCF is undesirable because it decomposes with time. For example, Fig. 1A (a) shows the spectrum of freshly prepared ZrO₂/SiO₂/HCF and Fig. 1A (b) and 1A (c) the spectra of the material aged for 30 and 60 days, respectively. An absorption band at about 740 nm, absent in the freshly prepared material, appears after 30 days and its intensity achieves a maximum after about 60 days. The surface of the freshly prepared solid which was colourless is now blue. The transition at 740 nm is assigned to the charge transfer in the Prussian Blue (PB) complex species². Fig. 1B shows the spectrum of ZrO₂/SiO₂/CuHCF, (a) for sample having Cu/Fe = 4.0 and (b) for a sample having Cu/Fe = 0.22. The absorption band at 480 nm in both samples is assigned to the charge transfer band Fe → Cu²⁷. In (b) an additional band is observed at 740 nm, due to the PB species, resulted from decomposition of HCF in excess on the surface of the sample.

Cyclic voltammetry studies

General features

Considering that the quantity of the electroactive species on the surface is very small, less than 1 mmol g⁻¹ for

Fe or Cu, and considering that the specific surface area is 420 m² g⁻¹, the surface density is lower than 2 atoms of Fe or Cu per nm². Therefore, if the mixed valence complex on the surface has a structure similar to that of bulk phase complex, it must be dispersed on the surface as aggregates forming various small islands.

In Fig. 2 the cyclic voltammetry waves for ZrO₂/SiO₂/HCF are shown, (A) for a freshly prepared sample and (B) for an aged sample. The midpoint potential, E_m , [$E_m = (E_{\text{pa}} + E_{\text{pc}})/2$, where E_{pa} and E_{pc} are the anodic peak potential and cathodic peak potential, respectively] is observed at $E_m = 0.21$ V for both samples. For the aged sample (B), a new redox couple is observed at about $E_m = 0.70$ V, due to the formation of the PB species²⁸.

Adding the freshly prepared ZrO₂/SiO₂/HCF to a Cu(II) solution, the new phase ZrO₂/SiO₂/CuHCF is formed on the surface. Figure 3 shows the CV waves for the sample with Cu/Fe = 4.0, and for the sample with Cu/Fe = 0.22. In (A) one redox couple is observed at $E_m = 0.69$ V while in (B), in addition to this midpoint potential, redox pairs at about $E_m = 0.90$ V and $E_m = 0.21$ V are observed. The first is due to the PB species and the second to the HCF species. The CV wave in (A) does not change with time even when cycling the potential over a long period, demonstrating that ZrO₂/SiO₂/CuHCF is very stable.

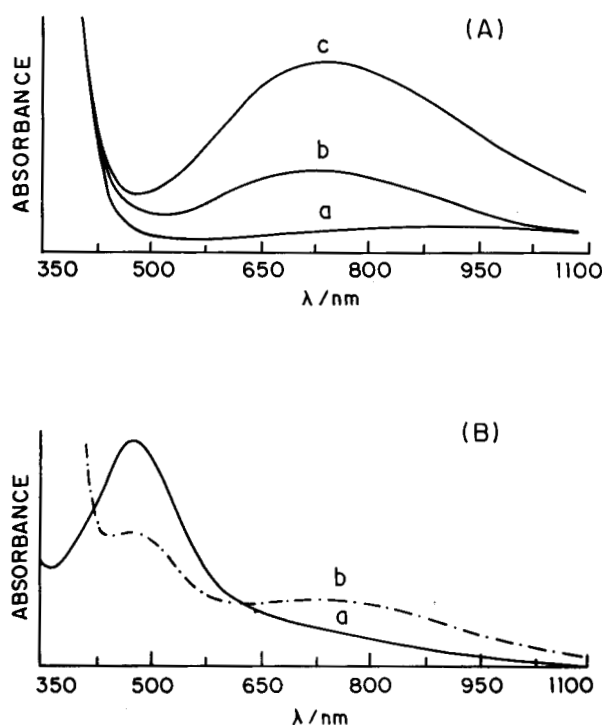


Figure 1. (A) Electronic absorption spectra of ZrO₂/SiO₂/HCF: a) freshly prepared material, b) material aged for 30 days, c) material aged for 60 days; (B) Electronic absorption spectra of ZrO₂/SiO₂/CuHCF a) Cu/Fe = 4.0, b) Cu/Fe = 0.22.

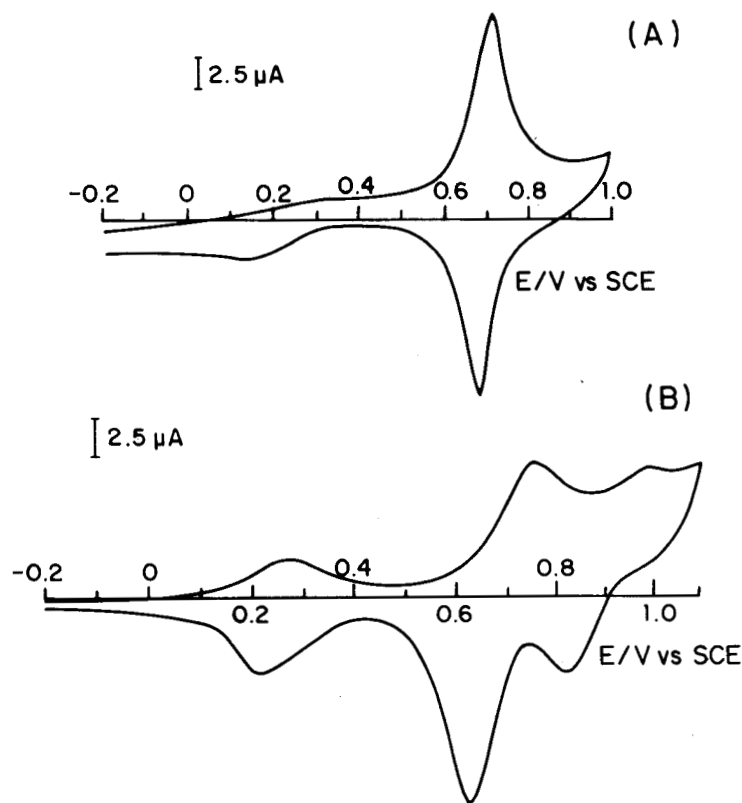


Figure 2. Cyclic voltammetry for $\text{ZrO}_2/\text{SiO}_2/\text{HCF}$, supporting electrolyte 1M KNO_3 and scan rate of 20 mV s^{-1} : (A) freshly prepared materia, l (B) aged for 30 days.

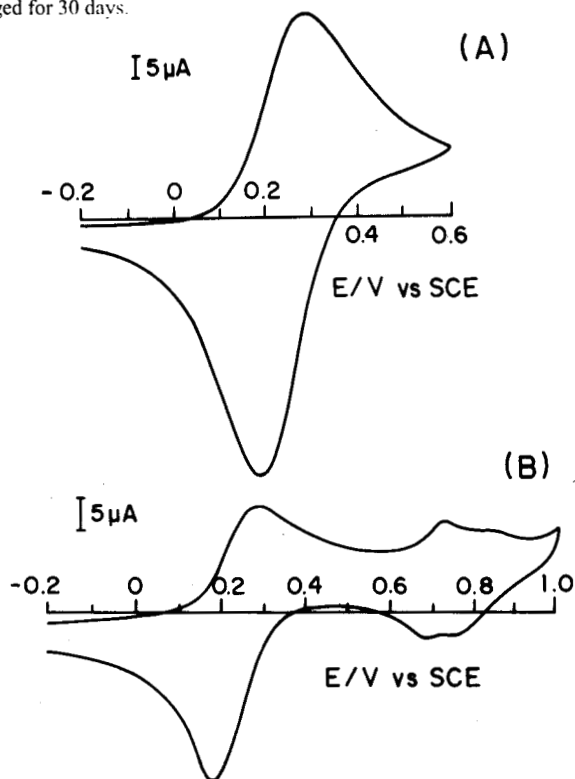
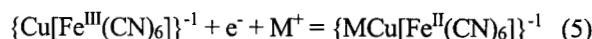


Figure 3. Cyclic voltammetry for $\text{ZrO}_2/\text{SiO}_2/\text{CuHCF}$, supporting electrolyte 1M KNO_3 and scan rate of 20 mV s^{-1} : (A) $\text{Cu}/\text{Fe} = 4.0$, (B) $\text{Cu}/\text{Fe} = 0.22$.

The nature of the supporting electrolyte

As evidence that CuHCF on the porous surface is agglomerated and structurally well-defined, the electrochemical response as the supporting electrolyte change. In Figure 4 the CV curves obtained in the following supporting electrolyte solutions are shown: A) KCl (a), NH_4Cl (b); B) LiCl (a) and NaCl (b). The redox peak potentials are well defined for KCl ($E_m = 0.69 \text{ V}$) and NH_4Cl ($E_m = 0.75 \text{ V}$), while for LiCl and NaCl they are not. It is well known that when electrodes of PB and their analogues are added to a supporting electrolyte solution, the cation M^+ moves into and out of the zeolitic type cavity of the complex during the redox process, according to the reaction:



Therefore the diameter of the zeolitic type cavity plays an important role in determining the formal potential of the above reaction according to the greater or lesser difficulty of the cation move into or out of the substrate structure. For copper hexacyanoferrate complex, the diameter of the cavity is 0.32 nm and the diameters of the hydrated ions are: $\text{Li}^+ = 0.42 \text{ nm}$, $\text{Na}^+ = 0.36 \text{ nm}$, $\text{K}^+ = 0.24 \text{ nm}$, and $\text{NH}_4^+ = 0.24 \text{ nm}$ ^{4,24,29,30}. Therefore it is clear that Li^+ and Na^+ , having larger diameters than the diameter of the cavity, will have difficulty moving into the zeolitic type structure of the complex for the reduction process.

The dependence of the peak potentials on supporting electrolyte concentrations was studied for K^+ and NH_4^+ ions. Plotting E_m vs. $-\log [\text{M}^+]$, a straight line in the concentration range of 0.05 and 1 M was observed for both ions (Fig. 5). The slopes of both lines are 50 mV for K^+ and 53

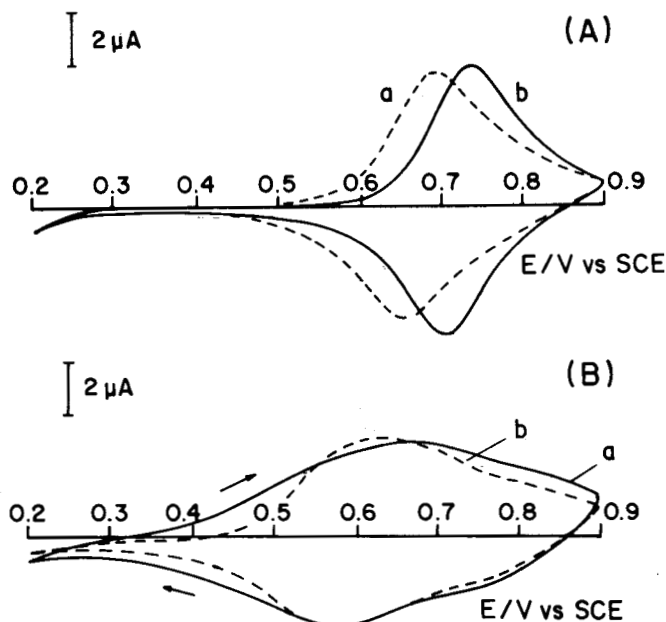


Figure 4. Cyclic voltammetry in 1 M supporting electrolyte solutions and scan rate of 20 mV s^{-1} for $\text{ZrO}_2/\text{SiO}_2/\text{CuHCF}$: (A) KCl (a), and NH_4Cl (b); (B) NaCl (a), and LiCl (b).

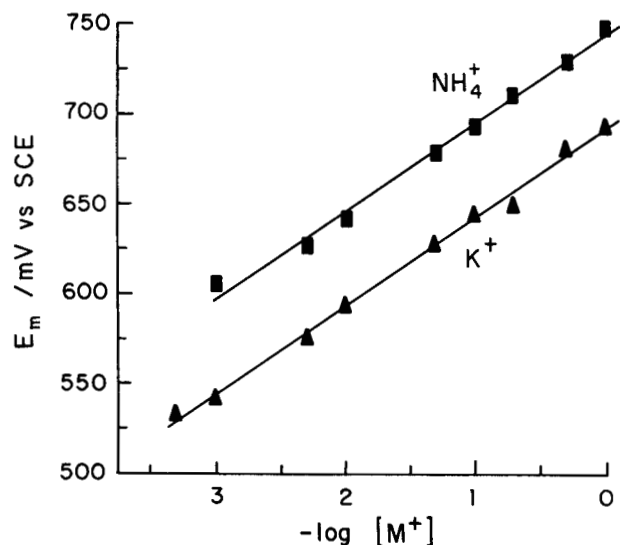


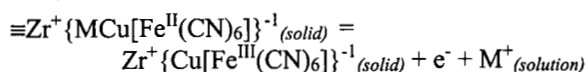
Figure 5. Plot of E_m vs. $-\log [M^+]$. Scan rate of 20 mV s^{-1} .

mV for NH_4^+ per decade of M^+ concentration change, both therefore being very close to the 59 mV required for Nernstian behavior.

The midpoint potential also depends on the nature of the ion, since despite the fact that K^+ and NH_4^+ hydrated diameter sizes are the same, the values of E_m are 0.69 and 0.75 V respectively. An experiment carried out in a mixture of KCl and NH_4Cl solution for which the total concentration was maintained constant (1M) shows how the midpoint potential changes as the molar fraction is varied (Fig. 6). With the increasing molar fraction of NH_4^+ the peak potential gradually increases. Therefore, the geometrical parameter (size of the cavity) is not the only factor which determines the potential shift, but the interaction of the cation with the surface site responsible for its adsorption must also be considered. The dependence of the midpoint potential on the nature of the cation can be described by the equation²¹:

$$E_m = E_s^0 + 0.059 \log [C] \quad (6)$$

where $E_s^0 = E^0 - 0.059 \log K$, and K is the equilibrium constant of the reaction at the solid-solution interface:



expressed as:

$$K = [CuHCF_{ox}][M^+] / [CuHCF_{red}] \quad (7)$$

where $[CuHCF_{ox}]$ and $[CuHCF_{red}]$ are the concentrations of $\{Cu[Fe^{III}(CN)_6]\}^{-1}$ and $\{MCu[Fe^{II}(CN)_6]\}^{-1}$, respectively.

It is evident from Eq. 7 that the smaller the constant K , the greater is E_s^0 and consequently E_m , provided that the concentration C is the same.

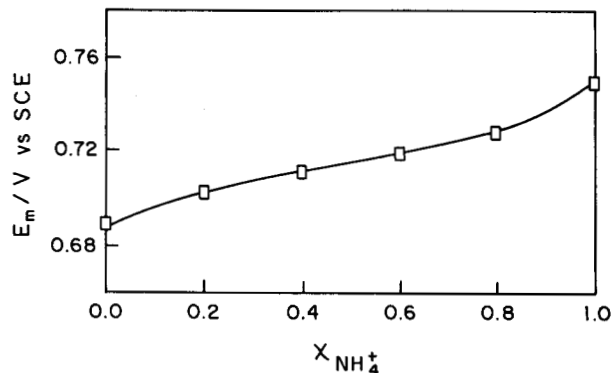


Figure 6. Change of E_m with molar fraction of NH_4^+ . $[NH_4^+] + [K^+] = 1 \text{ M}$.

Conclusions

Highly dispersed particles of copper hexacyanoferrate on silica gel surface coated with ZrO_2 are formed by reacting Cu^{2+} adsorbed on the solid surface with $[Fe(CN)_6]^{4-}$ or *vice versa*. The $ZrO_2/SiO_2/CuHCF$ electrode was chemically very stable in acid solution. The dependence of peak potentials on the nature of the cations is a result of the selective permeation according to their hydrated diameter sizes. The peak potential is also affected by the relative affinity of each cation to diffuse into the cavity and interact with the solid phase. Although SiO_2 is an insulating material, $ZrO_2/SiO_2/CuHCF$ is potentially useful for making electrochemical sensors for chemical analyses.

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